

Japanese Patent Application Laid-Open No. 11-106324

[Title of the Invention] Perfume-holding powder and composition containing the same

[Abstract]

An object of the invention is to provide a perfume-holding powder that is smaller in fluctuation of perfume-emitting velocity over time and allows retention of the perfume for a prolonged period of time perfume.

Provided are a perfume-holding powder characterized by containing a mesoporous powder containing silicon oxide as the primary component and a perfume held thereon, and a cosmetic containing the same.

[What is Claimed is]

[Claim 1] A perfume-holding powder characterized by containing a mesoporous powder containing silicon oxide as the primary component and a perfume held thereon.

[Claim 2] The perfume-holding powder according to Claim 1, wherein the mesoporous powder is a bulky powder having pores having a depth of 50 to 300 nm.

[Claim 3] The perfume-holding powder according to Claim 1, wherein the mesoporous powder is a rod-shaped powder containing pores having an external diameter of 20 to 200 nm and the pores are stretching in the length direction of the rod.

[Claim 4] The perfume-holding powder according to Claim 2, wherein the mesoporous powder is prepared by dissolving a silicate salt having a composition of $0 < \text{SiO}_2/\text{Y}_2\text{O}_3 < 2$ (Y: an alkali metal atom) in the presence of a cationic surfactant at pH 11 or more to a concentration of 0.1 to 1.2 M; adjusting the solution to a pH of 10.5 or less, thus forming a rod-shaped micelle with the cationic surfactant and allowing the silicic acid to condensate on the rod-shaped micelle; and removing the cationic surfactant from the micellar condensate having the silicate salt formed as the external shell by the condensation above.

[Claim 5] The perfume-holding powder according to Claim 3, wherein the mesoporous powder is prepared by dissolving a silicate salt having a composition of $0 < \text{SiO}_2/\text{Y}_2\text{O}_3 < 2$ (Y:

alkali metal atom) in the presence of a cationic surfactant at pH 11 or more to a concentration of 0.3 to 1.2 M; adjusting the solution to a pH of 10.5 or less within 30 minutes, thus forming a rod-shaped micelle with the cationic surfactant and allowing the silicic acid to condensate on the rod-shaped micelle; and removing the cationic surfactant from the micellar condensate having the silicate salt formed as the external shell by the condensation above.

[Claim 6] A composition, characterized by containing the perfume-holding powder according to any of Claims 1 to 5.

[Description of the Invention]

[0001]

[Technical Field] The present invention relates to a perfume-holding powder and a composition containing the same, in particular to improvement in perfume-holding mechanism by using a mesoporous powder as a holder.

[0002]

[Background Art] Various materials, for example perfumes, are volatile or easily deteriorated, and various methods have been employed for preserving these materials for an extended period. The methods include, for example, a method of dispersing and embedding a perfume in resin, a method of controlling the perfume vaporization rate by enclosing a perfume molecule in a material having openings such as cyclodextrin or the like. Materials produced by the former method is effective for preservation of the perfumes for indoor use but not appropriate, for example, for application to human. Alternatively, materials produced by the latter method, i.e., perfume clathrate materials, can be processed into the powder or paste form and are appropriate for application to human and others.

[0003]

[Problem to be Solved by the Invention] However, the method of using cyclodextrin or the like carried the problem of the change in perfume intensity over time. The present

invention is made in view of the problems associated with the conventional art, and an object of thereof is to provide a perfume-holding powder that is smaller in the change in perfume-emitting velocity over time and allows preservation of the perfume consistently for a prolonged period of time and a composition containing the same.

[0004]

[Summary of the Invention] After intensive studies to attain the object, the present inventors have found that it was possible to produce a mesoporous powder having minute micropores, i.e., having openings of 2 to 50 nm in diameter that was effective in preserving the perfume for an extended period of time and equalizing the emission velocity thereof by allowing a silicate salt having a particular silicon/alkali metal ratio to react at a particular concentration, and completed the present invention. The perfume-holding powder according to the present invention is characterized in that a silicon oxide is used as the base material for the perfume-holding powder and a perfume is held in the mostly uniform pores of the mesoporous powder for achieving the object.

[0005] In the present invention, the mesoporous powder preferably is a bulky powder having pores of 50 to 300 nm in depth. In addition in the present invention, the mesoporous powder is favorably a rod-shaped powder having an external diameter of 20 to 200 nm and the pores therein stretching in the length direction. In the present invention, the bulky powder is favorably produced by dissolving a silicate salt having a composition of $0 < \text{SiO}_2/\text{Y}_2\text{O} < 2$ (Y: alkali metal atom) in the presence of a cationic surfactant at pH 11 or more to a concentration of 0.1 to 1.2 M; adjusting the solution to a pH of 10.5 or less, thus forming a rod-shaped micelle with the cationic surfactant and allowing the silicic acid to condensate on the rod-shaped micelle; and removing the cationic surfactant from the micellar condensate having the silicate salt formed as the external shell by the condensation above.

[0006] In addition in the present invention, the rod-shaped powder is favorably produced by dissolving a silicate salt having a composition of $0 < \text{SiO}_2/\text{Y}_2\text{O} < 2$ (Y: alkali metal atom)

in the presence of a cationic surfactant at pH 11 or more to a concentration of 0.3 to 1.2 M; adjusting the solution to a pH of 10.5 or less within 30 minutes, thus forming a rod-shaped micelle with the cationic surfactant and allowing the silicic acid to condensate on the rod-shaped micelle; and removing the cationic surfactant from the micellar condensate having the silicate salt formed as the external shell by the condensation above. In addition, the composition according to the present invention is characterized by containing the perfume-holding powder above.

[0007]

[Best Mode for Carrying Out the Invention] Recognizing the possibility of the mesoporous powder containing silicon oxide as the primary component, the inventors have conducted the following tests. Namely, 0.5 mol (0.5 M) of sodium metasilicate (Na_2SiO_3) and 0.1 mol (0.1 M) of behenyltrimethylammonium chloride (BTC) were dissolved in 1 L of ion-exchange water. The solution was kept at a temperature of 70°C at the time, added with 2 N hydrochloric acid immediately after solubilization at a flow rate of 120 mL/min, and adjusted to a pH of 8 to 9. Then, the solution was filtered, and the filter cake was washed with water and baked at 700°C for 3 hours, to give a rod-shaped mesoporous powder.

[0008] A linalool (perfume) holder was prepared by using the rod-shaped mesoporous powder and β -cyclodextrin (β -CD). The holder was left in a thermostat oven at 40°C, and the linalool concentration in the headspace was determined by GC-MAS. Results are summarized in Fig. 1. The linalool concentration was expressed by its peak area value.

[0009] As apparent from the Fig., when linalool is placed alone, the headspace linalool concentration decreases rapidly with the passage of storage time. In contrast, when β -CD is used as a holder, the concentration decreases to the lowest after around 1 week, gradually increases since then for about one month, and then decreases as time further goes by. The change seems to be the result of the influence of decomposition or denaturation of β -CD rather than simply of the fluctuation in perfume vaporization rate.

On the other hand, when the rod-shaped mesoporous powder according to the present invention is used as a holder, the concentration reaches a steady state in about three days and does not vary significantly.

[0010] Further, noteworthy is the fact that when water is added to the perfume-holding powder according to the present invention, the perfume concentration in the headspace or the vaporization rate is increased drastically. Although still rather ambiguous, it seems to be because the mesoporous powder used in the present invention has micropores uniform in opening diameter; once a perfume is contained in the micropores, the contact area between the perfume and external air becomes almost identical with the micropore opening area independent of the change in the amount of the perfume added and thus the vaporization rate becomes constant; and the hydrophilicity of the internal surface of the micropores is relatively high, the perfume is replaced with water when water is injected, resulting in emission of the perfume outward from the micropores. The mesoporous powders particularly favorably used in the present invention are those prepared after examining the behavior of the water-soluble components obtained when silicic acid is dissolved in an alkali solution.

[0011] After studies, the inventors have found that it was possible to obtain an extremely uniform mesoporous powder by allowing silicate ions in the dissolved state at a ratio of $0 < \text{SiO}_2/\text{Na}_2\text{O} < 2$ to condensate onto quaternary ammonium salt micelles. When the $\text{SiO}_2/\text{Y}_2\text{O}$ ratio is greater than 2, the powder finally obtained undesirably has micropores lower in uniformity. For that reason, if a material having a $\text{SiO}_2/\text{Y}_2\text{O}$ ratio of more than 2 such as water glass is used, it is generally not possible to obtain a uniform mesoporous powder because of the difficulty in restoring the dissolved state due to white turbidity generated in the presence of a cationic surfactant. Although there is a report (JP-A No. 5-503499) on a method of forming a mesoporous powder from a composition having a $\text{SiO}_2/\text{Y}_2\text{O}$ ratio of 2 or more, the method is aimed at producing a mesoporous powder essentially containing an aluminium compound additionally and thus it is unfavorable

because of the concern about the possibility of denaturation of the perfume by the catalytic action of the aluminum compound. It is possible to produce a bulky or rod-shaped mesoporous powder when the silicate salt concentration is in a particular range, and rod-shaped mesoporous powder is particularly preferable among them from the viewpoint of perfume-holding capacity.

[0012] Hereinafter, favorable embodiments of the present invention will be described separately.

Silicate salt

The silicate salt for use in production of the mesoporous powder according to the present invention has a ratio of $0 < \text{SiO}_2/\text{Y}_2\text{O} < 2$ (Y: an alkali metal atom), and Na or K is particularly favorable as the alkali metal atom from the point of availability. The silicate salts can be produced by allowing various "silicon-containing materials" to react with an alkali, for example, NaOH. Examples of the "silicon-containing materials" include silicon oxide, silicate salts, silicon alkoxides, water glasses, and the like. Examples of the silicate salts include Na_2SiO_3 , Na_4SiO_4 , and the like.

[0013] Examples of the silicon alkoxides include tetramethyl orthosilicate, tetraethyl orthosilicate, and the like, and the alkoxides are favorably used as a mixture, for example with a silicate salt, because the reactivity thereof is lower alone. Examples of the water glasses include those of JIS No. 1, JIS No. 2, JIS No. 3, and the like. Most of these "silicon-containing materials" have a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of more than 2.0 and thus do not allow production of a uniform mesoporous powder because it is not possible to preserve the dissolved state in the presence of the cation surfactant described below. Thus, it is necessary to obtain a silicate salt at a ratio in the range of $0 < \text{SiO}_2/\text{Y}_2\text{O} < 2$ by solubilizing the silicon-containing materials by adding, for example, an alkali agent such as sodium hydroxide.

[0014] The silicate salt according to the present invention has the ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ less than 0.5, allows production of a mesoporous powder but leads to increase in cost due to

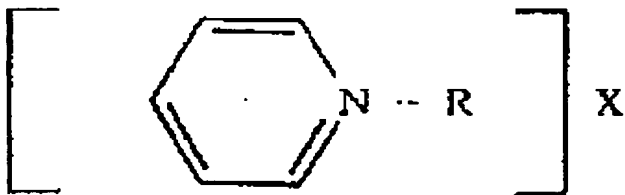
overuse of the alkali agent. Alternatively, if the ratio $\text{SiO}_2/\text{Na}_2\text{O}$ is 2 or more, the aqueous solution becomes more turbid in white and less dissolved, making it more difficult to provide a uniform mesoporous powder. For that reason, a ratio of $0 < \text{SiO}_2/\text{Y}_2\text{O} < 2$ is preferred and a ratio of $0.5 \leq \text{SiO}_2/\text{Y}_2\text{O} \leq 1.9$ is particularly preferable in the present invention

[0015] Cationic surfactant

On the other hand, a quaternary ammonium salt is favorable as the cationic surfactant. Examples of the quaternary ammonium salts include quaternary alkylammonium salts, $[\text{R}_4\text{N}] \text{X}$ and cyclic quaternary ammonium salts represented by the following Formula.

[0016]

[Formula 1]



Examples of the ammonium salts represented by the Formula above include those wherein R represents H, an alkyl group, an allyl group, benzyl group, phenyl group, hydroxyl group, or an hydroxyalkoxyl group; and X represents Cl^- , Br^- , I^- , and NO_3^- .

[0017] These quaternary ammonium salts should form a micelle when the aqueous solution is adjusted to a pH of 10.5 or less. It is particularly easier to produce a rod-shaped mesoporous powder when R of the quaternary ammonium salt above is an alkyl group having more than 18 carbons. It is also easier to produce a rod-shaped mesoporous powder in the presence of 0.1 to 3 M solution of a salt (e.g., NaCl or the like) having a counter anion other than silicate anion, such as Cl^- , Br^- , or I^- when R of the quaternary ammonium salt is an alkyl group having 18 carbons or fewer. The method of producing a mesoporous powder characteristic to the present invention comprises the following steps:

[0018] Solubilization step

A silicate salt and a cationic surfactant are mixed and heated to the room temperature or the temperature that the mixture is dissolved. If the pH during mixing is 11 or less or the ratio $\text{SiO}_2/\text{Na}_2\text{O}$ is more than 2, an alkali agent is added until the pH becomes 11 or more and the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio less than 2. The period for solubilization is relatively short at a period required for heating until the two components are solubilized.

[0019] The molar ratio of the cationic surfactant to the silicate salt is preferably 0.02 to 1.0 and particularly preferably 0.05 to 0.3. If the molar ratio of the cationic surfactant to the silicate salt is less than 0.02, the amount of the produced rod-shaped micelles of the cationic surfactant decreases, while if the molar ratio is over 1.0, unreacted cationic surfactant remains wastefully in a greater amount.

[0020] Condensation step

The solution prepared in the solubilization step above is adjusted to a pH of 10.5 or less by addition of an acid. As a result, the cationic surfactant or the spherical micelles thereof aggregate to form rod-shaped micelles. In addition, the silicate ions in the dissolved state at pH 11 or more aggregates at a pH of 10.5 or less, depositing silicic acid on the external surface of the rod-shaped micelles of the cationic surfactant.

[0021] Surfactant-removing step

After the dispersion containing the condensed powder is filtered, the cationic surfactant contained in the powder is removed. The surfactant is removed, for example, by washing with water, baking, or the like. The cationic surfactant is removed in this removal processing, leaving a mesoporous powder.

[0022] Examination of the ratio $\text{SiO}_2/\text{Y}_2\text{O}$

First, the ratio $\text{SiO}_2/\text{Y}_2\text{O}$ characteristic to the present invention is examined. A suitable amount of analytical grade sodium hydroxide (manufactured by Nakarai Tesque, Inc.) is dissolved in 1 L of ion-exchange water; 300 g of commercial silicon dioxide (#200, manufactured by Aerosil) is added thereto; and the mixture is stirred. The dispersion

was baked at 700°C for 5 hours, to give sodium silicate. Then, the inventors produced various sodium silicates at the ratios of SiO₂/Na₂O shown in Table 1 and tried to produce mesoporous powders by using them as the starting material.

[0023]

[Table 1]

SiO ₂ /Na ₂ O	0.5	1.0	1.5	2.0
PH	12.05	11.95	11.65	11.35
Dissolved state	Complete solubilization	Complete solubilization	Complete solubilization	Translucent
Specific surface area	1066	1126	1142	1052

[0024] X-ray diffraction measurement was also performed. The measurement was performed at a speed of two degrees (2θ) per minute by using JDX-350 manufactured by JEOL and a CuKα ray as the X-ray source. The slit width was 1 degree-0.2 mm-1 degree. The results showed that the sodium silicate was in the dissolved state, and the results by X-ray diffraction that the sodium silicate had a hexagonal structure. However, when sodium silicate was not completely dissolved, the hexagonal structure was not formed occasionally, prohibiting production of the mesoporous powder having uniform micropores.

[0025] As apparent from the Table above, the ratio SiO₂/Na₂O is preferably less than 2.0, and thus use, for example, of water glass or the like having a ratio of 2.0 or more does not allow production of a suitable mesoporous powder. A ratio SiO₂/Na₂O up to approximately 1.9 was particularly favorable for forming the hexagonal structure consistently and producing uniform micropores.

[0026] Silicate salt concentration

In the present invention, it is favorable to adjust the concentration of silicate salt for

equalizing the mesoporous powder. A certain mole of sodium metasilicate and a certain mole of behenyltrimethylammonium chloride (BTC) were dissolved in 1 L of ion-exchange water. The temperature of the solution was kept at 70°C; immediately after solubilization, an aqueous 2 N hydrochloric acid solution was added thereto at a speed of 120 mL/min; and the pH of the solution was adjusted to 8 to 9. Then, the solution was filtered and the filter cake was washed and baked at 700°C for 3 hours, to give a powder.

[0027]

[Table 2]

Meta silicate concentration (M)	0.15	0.5	1.0	1.5
BTC (M)	0.03	0.1	0.2	0.3
Aspect	Bulky	Rod-shaped mesoporous	Rod-shaped mesoporous	Rod-shaped nonporous
	Fig. 2	Fig. 3	Fig. 4	Fig. 5

[0028] As apparent from the results, the solution containing silicic acid at a concentration of 0.15 M gave a bulky mesoporous powder. The solution at 1.5 M tended to give a rod-shaped powder, which had almost no openings. Studies by the inventors confirmed that a solution at a silicate salt concentration of 0.1 to 0.5 M gave a bulky mesoporous powder and a solution at 0.3 to 1.2 M a rod-shaped mesoporous powder. Solutions having a silicate salt concentration in the range of 0.3 to 0.5 M gave a mixture of these forms, and the abundance ratio between them varied depending on other conditions described below.

[0029] From the results above, the silicic acid concentration is preferably 0.1 to 1.2 M for production of a mesoporous powder in the present invention and 0.3 to 1.2 M for production of a rod-shaped mesoporous powder.

[0030] Addition rate of the acid for pH adjustment

For production of mesoporous powders in the present invention, the addition rate of the acid added in the condensation step for pH adjustment is favorably controlled. In the similar way as above, 0.5 mole of sodium metasilicate and 0.1 mole of behenyltrimethylammonium chloride (BTC) were dissolved in 1 L of ion-exchange water (pH 11.5). The temperature of the solution was kept at 70°C; immediately after solubilization, an aqueous 2 N hydrochloric acid solution was added thereto; and the pH of the solution was adjusted to 9. The addition rate of 2 N-hydrochloric acid was changed during addition. Then, the solution was filtered and the filter cake was washed and baked at 700°C for 3 hours, to give a powder.

[0031]

[Table 3]

Hydrochloric acid addition rate	2 mL/min	120 mL/min
Period needed for pH change	150 min	2.5 min

Aspect	Bulky mesoporous	Rod-shaped mesoporous
	Fig. 6	Fig. 3

[0032] As apparent from the results, a bulky mesoporous power was obtained at an 2 N-hydrochloric acid addition rate of 2 mL/min, while a rod-shaped mesoporous powder was obtained at 120 mL/min. Further detailed studies showed that in order to obtain a rod-shaped mesoporous powder particularly preferable in the present invention, the hydrochloric acid addition rate under the condition above was favorably 10 mL/min (period needed for pH change: 30 min or less).

[0033] Concentration of the acid for pH adjustment

In the present invention, it is favorable to control the concentration of the acid for pH adjustment added in the condensation step in order to produce a powder, in particular a favorable rod-shaped powder. In the similar way as above, 0.5 mole of sodium metasilicate and 0.1 mole of behenyltrimethylammonium chloride (BTC) were dissolved in 1 L of ion-exchange water (pH11.5). The temperature of the solution was kept at 70°C; immediately after solubilization, an aqueous 2 N hydrochloric acid solution was added thereto at a speed of 120 mL/min; and the pH of the solution was adjusted to 9. Then, the solution was filtered and the filter cake was washed and baked at 700°C for 3 hours, to give a powder.

[0034]

[Table 4]

Hydrochloric acid addition rate	0.2N	2 N	5 N
Period needed for pH change	35 min	2.5 min	1 min
Aspect	Bulky Mesoporous Fig. 7	Rod-shaped mesoporous Fig. 3	Rod-shaped mesoporous Fig. 8

[0035] As apparent from the results, a bulky mesoporous powder was obtained when 0.2 N-hydrochloric acid was used, while a rod-shaped mesoporous powder when 2 N or higher hydrochloric acid was used. A pH adjustment period of 30 min or more also resulted in a bulky powder, while a period of 30 min or less more likely resulted in a rod-shaped powder. In particular, a rod-shaped mesoporous powder, when used as the perfume-holding powder according to the present invention, exerted an excellent perfume-holding action; and for that reason, the rod-shaped mesoporous powder is preferable.

[0036] Then, deodorant powders shown in the following Table 5 were prepared, and the

technical merits of the perfume-holding powders according to the present invention were examined. In either case, the perfume concentration was adjusted to be 1% in the composition.

[Table 5]

	Test No. 1	Test No. 2	Test No. 3	Test No. 4
Perfume				
Perfume-holding powder	5.0			
Perfume-holding silica gel		5.0		
Perfume-holding cyclodextrin			5.0	
Pure perfume				1.0
Ordinary powder				
Aluminium chlorohydrate	5.0	5.0	5.0	5.0
Zinc oxide	5.0	5.0	5.0	5.0
Talc	80.0	80.0	80.0	84.0
Oil				
Liquid paraffin	5.0	5.0	5.0	5.0
Technical merits				
Scent of product (after 3 days)	+	++	++	+++
Scent of product (after 1 month)	+	+	++	+
Scent during use (after 1 month)	+++	+	++	+

[0037] In production of each test deodorant powder, respective powders were fed into and blended uniformly in a Henschel Mixer; then other components were added; and then the mixture was stirred uniformly. The resulting mixture was pulverized in an atomizer and press-molded in a container, to give a deodorant powder. The powders thus obtained were stored at room temperature in openness.

[0038] As apparent from the results above, the deodorant powders employing the perfume-holding powder according to the present invention do not emit the scent of product so intensely and preserve a faint scent condition, but emit a rather intense scent, replacing the sweat or sebum on the skin during use. In addition, the deodorant powder according to the present invention was effective in sebum absorption, favorably suppressing the greasy feeling after use.

[0039] Next, the present inventors have examined the ratio of the mesoporous powder to the perfume and the technical merits thereof.

[Table 6]

Formulation	No. 5	6	6	7	8	9	10	11	12
Mesoporous powder	0.01	0.1	0.5	1.0	5.0	10.0	30.0	50.0	80.0
Perfume	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ordinary powder									
Aluminium chlorohydrate	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Talc	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Oil									
Liquid paraffin	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0

Scent

Immediately after production	++	++	++	+	+	+	+	+	+
After 1 month	+	+	+	+	+	+	+	+	+
During use	++	++	+++	+++	+++	+++	+++	++	++

[0040] As apparent from the Table 6 above, formulations containing 0.01 to 0.1 part by weight of mesoporous powder with respect to 1 part by weight of perfume, although they can be pulverized satisfactorily, often lead to more intense vaporization of the perfume during storage, resulting in slight decrease in the intensity of the scent during use, although the intensity was still in the practical range. In addition, when the mesoporous powder is contained in an amount of more than 30 parts by weight, the scent intensity seems to decline, probably because there are too many openings in the mesoporous powders. Therefore, the blending ratio of the perfume to the mesoporous powder is preferably approximately 1:0.5 to 1:30 by weight. The mesoporous powder according to the present invention is effective in preventing exfoliation of the powder due to its superior oil and water adsorption properties.

[0041] In the present invention, for production of a perfume-holding powder, it is only necessary to blend a liquid or liquefied perfume with the mesoporous powder obtained in the manner described above. It is also favorable to hydrophobilize or hydrophilize the surface of the mesoporous powder according to the kinds of the materials used or the formulations wherein the perfume-holding powder is formulated,

[0042]

[EXAMPLE] Hereinafter, the present invention will be described in detail with reference to EXAMPLEs.

EXAMPLE 1

Production of bulky mesoporous powder

To a solution of 400 g of analytical grade sodium hydroxide (manufactured by Nakarai Tesque, Inc.) in 1 L of ion-exchange water, added was 300 g of commercial silicon dioxide (#200, manufactured by Aerosil), and the mixture was stirred. The dispersion was baked at 700°C for 5 hours, to give sodium silicate (NaSiO_3). Then, 0.5 mol of sodium silicate and 0.1 mol of stearyltrimethylammonium chloride were added to 1 L of ion-exchange water and dissolved therein at 50°C. The pH of the solution was 11.8. The solution was further adjusted to pH 8.5 by gradual addition of 2 N-HCl. The solution was further filtered, and the filter cake was washed with water repeatedly for 5 times, then washed with acetone, and dried. The dried powder was baked at 700°C for 5 hours, to give a bulky mesoporous powder.

[0043] EXAMPLE 2

Production of bulky mesoporous powder

0.5 mol of commercially available anhydrous sodium metasilicate (manufactured by Nakarai Tesque, Inc.) and 0.1 mol of stearyltrimethylammonium chloride were added to 1 L of ion-exchange water and dissolved therein at 70°C. The pH of the solution was 11.75. The solution was further adjusted to pH 8.5 by gradual addition of 2 N-HCl. The solution was further filtered, and the filter cake was washed with water repeatedly 5 times, then washed with acetone and dried. The dried powder was baked at 700°C for 5 hours, to give a bulky mesoporous powder. Fig. 9 is a TEM photograph of the bulky mesoporous powder obtained in the manner described above. The Fig. shows openings stretching in parallel in the powder, and further observation in an analogous manner revealed that the opening depth in the present invention was 50 to 300 nm.

[0044] EXAMPLE 3

Production of bulky mesoporous powder

To a solution of 30 g of analytical grade sodium hydroxide (manufactured by Nakarai Tesque, Inc.) dissolved in 1 L of ion-exchange water, 30 g of commercial silicon dioxide

(#200, manufactured by Aerosil) was added, and the mixture was stirred. 0.1 mol of stearyltrimethylammonium chloride was added to and dissolved in the solution at 70°C. The pH of the solution was 11.5. The solution was further adjusted to pH 8.5 by gradual addition of 2 N-HCl. The solution was further filtered and the filter cake was washed with water repeatedly 5 times and then washed with acetone and dried. The dried powder was baked at 700°C for 5 hours, to give a bulky mesoporous powder. The X-ray diffraction pattern of the mesoporous powder thus obtained is shown in Fig. 10, the nitrogen adsorption isotherm in Fig. 11, and the distribution of opening diameters in Fig. 12, respectively.

[0045] The X-ray diffraction pattern shown in Fig. 10 shows four diffraction peaks indicating a hexagonal structure. In addition, the sharp rise at a relative vapor pressure (P/p_0) of around 0.35 in the nitrogen adsorption isotherm shown in Fig. 11 indicates the uniformity of opening diameter and, more specifically, the opening diameter distribution shown in Fig. 12.

[0046] Next, an X-ray diffraction pattern of a mesoporous powder prepared in an analogous manner except that the sodium hydroxide was replaced with an equimolar amount of potassium hydroxide is shown in Fig. 13. The Fig. reveals that any alkalis other than sodium hydroxide may be used for production of the mesoporous powder according to the present invention.

[0047] EXAMPLE 4

Production of bulky mesoporous powder

0.5 mol of commercially available anhydrous sodium metasilicate (Nakarai Tesque, Inc.) and 0.1 mol of cetyltrimethylammonium chloride was added to and dissolved in 1 L of ion-exchange water at 70°C. The pH of the solution was 11.84. The solution was further adjusted to pH 8.5 by gradual addition of 2 N-HCl. The solution was additionally filtered and the filter cake was washed with water repeatedly 5 times and then washed with acetone and dried. The dried powder was baked at 700°C for 5 hours, to give a bulky

mesoporous powder.

[0048] EXAMPLE 5

Production of bulky mesoporous powder

0.5 mol of commercially available anhydrous sodium metasilicate (Nakarai Tesque, Inc.) and 0.5 mol of lauryltrimethylammonium chloride were added to and dissolve in 1 L of ion-exchange water at 70°C. The pH of the solution was 11.92. The solution was further adjusted to pH 8.5 by gradual addition of 2 N-HCl. The solution was additionally filtered and the filter cake was washed with water repeatedly 5 times and then washed with acetone and dried. The dried powder was baked at 700°C for 5 hours, to give a bulky mesoporous powder.

[0049] EXAMPLE 6

Production of bulky mesoporous powder

0.5 mol of commercially available sodium orthosilicate (Nakarai Tesque, Inc.), 0.1 mol of stearyl trimethylammonium chloride, and 0.1 mol of phenyltrimethylammonium chloride were added to and dissolved in 1 L of ion-exchange water at 70°C. The pH of the solution was 12.05. The solution was further adjusted to pH 8.5 by gradual addition of 2 N-HCl. The solution was further filtered and the filter cake was washed with water repeatedly 5 times and then washed with acetone and dried. The dried powder was baked at 700°C for 5 hours, to give a bulky mesoporous powder.

[0050] EXAMPLE 7

Production of bulky mesoporous powder

0.5 mol of stearyl trimethylammonium chloride was added to and dissolved in a liquid mixture of 500 g of commercially available water glass ($\text{SiO}_2/\text{Na}_2\text{O}$: 2.0) and 500 g of ion-exchange water at 70°C. The pH of the solution was 11.68. The solution was further adjusted to pH 8.5 by gradual addition of 2 N-HCl. The solution was additionally filtered and the filter cake was washed with water repeatedly 5 times and then washed with acetone and dried. The dried powder was baked at 700°C for 5 hours, to give a bulky

mesoporous powder.

[0051] EXAMPLE 8

Production of bulky mesoporous powder

30 g of SiO₂ and 0.1 mol of stearyltrimethylammonium chloride were dispersed in 1 L of ion-exchange water and then dissolved by addition of 2 g of NaOH, and the mixture was stirred at 70°C for 3 hours. The pH of the solution was 11.23. The solution was further adjusted to pH 8.5 by gradual addition of 2 N-HCl. The solution was additionally filtered and the filter cake was washed with water repeatedly 5 times and then washed with acetone and dried. The dried powder was baked at 700°C for 5 hours, to give a bulky mesoporous powder.

[0052] Physical properties of the mesoporous powder prepared in each EXAMPLE above are summarized in the following Table 7.

[Table 7]

	$d_{100}(\text{\AA})$	$a_0(\text{\AA})$	S.S.A (m^2/g)	Total Pore Volume (cc)
EXAMPLE 1	36.78	42.47	1125	2.06
EXAMPLE 2	38.38	44.32	1074	1.73
EXAMPLE 3	35.31	40.77	1210	1.84
EXAMPLE 4	34.62	39.98	1165	1.01
EXAMPLE 5	33.31	38.46	637	0.51
EXAMPLE 6	36.78	42.47	1077	2.32
EXAMPLE 7	37.56	43.37	1220	1.22
EXAMPLE 8	36.03	41.61	1242	1.01

[0053] EXAMPLE 9

Preparation of rod-shaped mesoporous powder

0.5 mol of sodium metasilicate (Na_2SiO_3) and 0.1 mol of behenyltrimethylammonium chloride (BTC) were dissolved in 1 L of ion-exchange water. The temperature of the solution was kept at 70°C , and immediately after solubilization, the solution was adjusted to pH 8 to 9 by addition of 2 N hydrochloric acid at a flow rate of 120 mL/min. Then, the solution was filtered, and the filter cake was washed with water and baked at 700°C for 3 hours. The X-ray diffraction pattern of the rod-shaped mesoporous powder thus obtained is shown in Fig. 14, the nitrogen adsorption isotherm in Fig. 15, and the distribution of opening diameters in Fig. 16, respectively.

[0054] The results of X-ray diffraction in Fig. 14 show four diffraction peaks indicating a hexagonal structure. In addition, the steep rise at a relative vapor pressure (P/p_0) of around 0.45 in the nitrogen adsorption isotherm shown in Fig. 15 indicates the uniformity of opening diameter, more specifically, the opening diameter distribution shown in Fig. 16. Properties of the bulky and rod-shaped mesoporous powders produced in similar method are compared as follows:

[0055]

[Table 8]

	Bulky mesoporous powder	Rod-shaped mesoporous powder
Na_2SiO_3	0.5 mol/l	0.5 mol/l
Specific surface area	1,100 m^2/g	900 m^2/g
Oil adsorption amount	300 mL/100 g	500 mL/100 g
Micropore diameter	30A	35A

As apparent from the Table 8 above, the rod-shaped mesoporous powder has a specific

surface smaller than that of the bulky mesoporous powder, but has a larger oil adsorption capacity and thus an excellent oil adsorption property.

[0056] EXAMPLE 10

Preparation of rod-shaped mesoporous powder

0.5 to 1.2 mol of sodium metasilicate (Na_2SiO_3) and 0.05 to 0.24 mol of behenyltrimethylammonium chloride (BTC) were dissolved in 1 L of ion-exchange water. The temperature of the solution was kept at 70°C, and immediately after solubilization, the solution was adjusted to pH 8 to 9 by addition of 2 N hydrochloric acid. Then, the solution was filtered, and the filter cake was washed with water and baked at 700°C for 3 hours, to give a rod-shaped mesoporous powder. The ratio $\text{Na}_2\text{SiO}_3/\text{BTC}$ was 1/0.1 or 1/0.2. In this range, it was possible to prepare a rod-shaped mesoporous powder in either case.

[0057] EXAMPLE 11

Preparation of rod-shaped mesoporous powder

0.5 to 1.2 mol of sodium metasilicate (Na_2SiO_3), 0.05 to 0.24 mol of stearyltrimethylammonium chloride (STC), and 0.5 to 2 mol of sodium chloride (NaCl) were dissolved in 1 L of ion-exchange water. A rod-shaped mesoporous powder was prepared hereinafter in a similar manner to EXAMPLE 10. The ratio $\text{Na}_2\text{SiO}_3/\text{STC}/\text{NaCl}$ was 1/0.1/1 to 4 or 1/0.2/1 to 2. In this range, it was possible to prepare a rod-shaped mesoporous powder in either case.

[0058] EXAMPLE 12

Preparation of rod-shaped mesoporous powder

0.5 to 1.2 mol of sodium metasilicate (Na_2SiO_3), 0.05 to 0.24 mol of stearyltrimethylammonium chloride (STC), and 0.5 to 2 mol of sodium bromide (NaBr) were dissolved in 1 L of ion-exchange water. A rod-shaped mesoporous powder was prepared hereinafter in a similar manner to EXAMPLE 10. The ratio of $\text{Na}_2\text{SiO}_3/\text{STC}/\text{NaBr}$ was 1/0.1/1 to 4 or 1/0.2/1 to 2. In this range, it was possible to

prepare a rod-shaped mesoporous powder in either case.

[0059] EXAMPLE 13

Preparation of rod-shaped mesoporous powder

0.5 to 1.2 mol of sodium orthosilicate (Na_4SiO_4) and 0.05 to 0.24 mol of behenyltrimethylammonium chloride (BTC) were dissolved in 1 L of ion-exchange water. A rod-shaped mesoporous powder was prepared hereinafter in a similar manner to EXAMPLE 10. The ratio of $\text{Na}_4\text{SiO}_4/\text{BTC}$ was 1/0.1 to 1/0.2. In this range, it was possible to prepare a rod-shaped mesoporous powder in either case.

[0060] EXAMPLE 14

Preparation of rod-shaped mesoporous powder

0.5 to 1.2 mol of sodium metasilicate (Na_2SiO_3), 0.05 to 0.24 mol of behenyltrimethylammonium chloride (BTC), and 0 to 0.5 mol of silicon dioxide (SiO_2) were dissolved in 1 L of ion-exchange water. A rod-shaped mesoporous powder was prepared hereinafter in a similar manner to EXAMPLE 10. The amount of Na_2SiO_3 and SiO_2 was less than 1.3 mol. In this range, it was possible to prepare a rod-shaped mesoporous powder in either case.

[0061] EXAMPLE 15

Preparation of rod-shaped mesoporous powder

0.5 to 1.2 mol of sodium metasilicate (Na_2SiO_3), 0.05 to 0.24 mol of stearyltrimethylammonium bromide (STB), and 0.2 to 2 mol of sodium bromide (NaBr) were dissolved in 1 L of ion-exchange water. A rod-shaped mesoporous powder was prepared hereinafter in a similar manner to EXAMPLE 10. The ratio of $\text{Na}_2\text{SiO}_3/\text{STB}/\text{NaBr}$ was 1/0.1/1 to 4 or 1/0.2/1 to 2. In this range, it was possible to prepare a rod-shaped mesoporous powder in either case.

[0062] The rod-shaped mesoporous powders produced according to the invention are extremely higher in oil adsorption efficiency as described above, and thus, when used as blended in external preparations for the skin such as cosmetics, improves the adhesiveness

to the skin by adsorbing the sebum adequately. The blending ratio of a perfume-holding powder to an external preparation for the skin when they are blended may optionally vary according to the form of the cosmetic, but is generally 0.1 to 80 wt %. The blending ratio thereof in emulsified or dispersed products is generally 0.1 to 10 wt %, while that in powdery or pressed powder products is generally 0.1 to 70 wt %.

[0063] In addition to the perfume-holding powder, other components commonly used in external preparations may be blended in the range in quality and quantity that does not impair the advantageous effects of the present invention. Examples of the additives include moisturizing agents, waxes, pigments, oils, surfactants, antiseptic materials, antioxidants, chelating agents, alkalis, water-soluble polymers, oil-soluble polymers, clay minerals, and the like. Hereinafter, typical cosmetic formulations containing the perfume-holding powder will be described as examples of the present invention.

[0064]

Formulation No. 1 Lipstick

Polyethylene wax	3%
Ceresin wax	10
Carnauba wax	2
Candelilla wax	5
Liquid paraffin	30
Castor oil	15
Di-2-heptylundecanoic acid glycerin	20
Olive oil	11
Red iron oxide	0.2
Red 202	1.8
Perfume-holding powder	2

<Production method> The oils and waxes were dissolved by heating at 85 to 90°C, and after addition of the pigments, the mixture was dispersed. The liquid was immediately

deaerated under reduced pressure, transferred into a predetermined container, and cooled, to give a lipstick. The lipstick was hardly removed after application.

[0065]

Formulation No. 2 Pressed eye shadow

Talc	26
Mica	35
Titanium-coated mica	20
Liquid paraffin	2.8
Dimethylpolysiloxane (6cs)	2
Perfume-holding powder	5
Sorbitan monooleate	1
Ultramarine	8
Red 201	0.2

<Production method> The powders above except titanium-coated mica were blended in a Henschel Mixer, and then, the oils and the surfactant were added thereto, and the mixture was pulverized in a pulverizer. Further, titanium-coated mica was added thereto, and the mixture was blended uniformly in the Henschel Mixer. The mixture was press molded in a predetermined shallow dish, to give an eye shadow.

[0066]

Formulation No. 3 Baby powder

Perfume-holding powder	40
Talc	58.7
Citric acid	0.2
Bengala	0.01
Liquid paraffin	1
Perfume	0.09

<Production method> A solution of citric acid in 99% alcohol was added to talc, and the

mixture was blended in a Henschel Mixer and then heated at 80°C for removal of alcohol. Other ingredients were added thereto, and the mixture was pulverized in an atomizer. The resulting powder was transferred into a predetermined container, to give a baby powder.

[0067]

Formulation No. 4 Emulsified foundation

Stearic acid	0.7
Isopropyl myristate	4
Squalane	22
Polyoxyethylene (10 mole) stearyl ether	2
Cetyl alcohol	0.3
Talc	7
Perfume-holding powder	3
Iron oxide pigment	2.5
Red 202	0.5
Antiseptic	0.09
Triethanolamine	0.42
Propylene glycol	5
Purified water	52.19
Perfume	0.3

<Production method> The oils and the surfactants were dissolved by heating, the pigments were added thereto, and the mixture was dispersed uniformly. Triethanolamine and propylene glycol dissolved and heated in purified water were added thereto, and the mixture was emulsified. The emulsion was cooled while stirred, added uniformly with the perfume, and filled into a container, to give an emulsified foundation.

[0068]

Formulation No. 5 Rouge

Talc	30
Mica	35
Titanium oxide	3
Titanium-coated mica	5.5
Red 202	0.5
Perfume-holding powder	3
Sorbitan diisostearate	1
Squalane	7
Methylphenylpolysiloxane	15

<Production method> The pigments were blended and added with other ingredients that were previously heated and dissolved, and the resulting mixture was blended and pulverized. The powder was molded in a shallow dish, to give a pressed rouge.

[0069]

Formulation No. 6 Liquid eye liner

Isoparaffin	58.97
Hydrocarbon resin	5
Carnauba wax	1
Candelilla wax	5
Cholesterol	2
Ethyl alcohol	5
Purified water	8
Organic-modified montmorillonite	3
Iron oxide black	10
Perfume-holding powder	1
Sorbitan monostearate	1
Perfume	0.03

<Production method> The activators, water, organic-modified montmorillonite and

pigment were added to part of isoparaffin, and the mixture was stirred and dispersed uniformly and heated to 85°C. The other isoparaffin, resins, and waxes were placed in a tank and dissolved uniformly by heating at 90°C. The dispersion previously prepared was added thereto, and the mixture was stirred and dispersed at 85°C to 90°C, added with the perfume, and cooled gradually to 30°C. The mixture was filled into a predetermined container, to give a water-resistant eyeliner.

[0070]

Formulation No. 7 Two-way foundation

Silicone-treated titanium oxide	20
Silicone-treated mica	22
Silicone-treated iron oxide	3
Perfume-holding powder	5
Liquid paraffin	4.5
Methylpolysiloxane (100cs)	25
Methyl hydrogen polysiloxane (20cs)	20
Sorbitan sesquioleate	0.5

<Production method> The pigments were uniformly blended and added with the oils and activators, and the resulting mixture was blended further. The mixture was pulverized in an atomizer and press molded in a predetermined shallow dish. As described above, the external preparations for the skin containing a perfume-holding powder are superior in perfume-holding properties and firmly attached to the skin, and thus provide a favorable feeling when used.

[0071]

[Advantageous Effect of the Invention] As described above, the perfume-holding powder according to the present invention and the composition including the same can hold a perfume consistently for an extended period of time and emit the perfume at a constant velocity, as the perfume is contained in the mesoporous powder containing silicon oxide as

the primary component and having uniform minute micropores.

[Brief Description of the Drawings]

[Fig. 1] A graph showing the perfume-holding action of a perfume-holding powder according to the present invention.

[Fig. 2] A photograph showing the relationship between silicate salt concentration (0.15 M) and crystalline state.

[Fig. 3] A photograph showing the relationship between silicate salt concentration (0.5 M) and crystalline state.

[Fig. 4] A photograph showing the relationship between silicate salt concentration (1.0 M) and crystalline state.

[Fig. 5] A photograph showing the relationship between silicate salt concentration (1.5 M) and crystalline state.

[Fig. 6] A photograph showing the relationship between addition rate of an acid for pH adjustment (2 mL/min) and crystalline state.

[Fig. 7] A photograph showing the relationship between concentration of an acid for pH adjustment (0.2 N) and crystalline state.

[Fig. 8] A photograph showing the relationship between concentration of an acid for pH adjustment (5.0 N) and crystalline state.

[Fig. 9] A TEM photograph showing the structure of a bulky mesoporous powder obtained in the present invention.

[Fig. 10] An X-ray diffraction pattern of a bulky mesoporous powder obtained in the present invention.

[Fig. 11] The nitrogen-adsorption isotherm of the mesoporous powder shown in Fig. 10.

[Fig. 12] A drawing showing the opening diameter distribution of the mesoporous powder shown in Fig. 10.

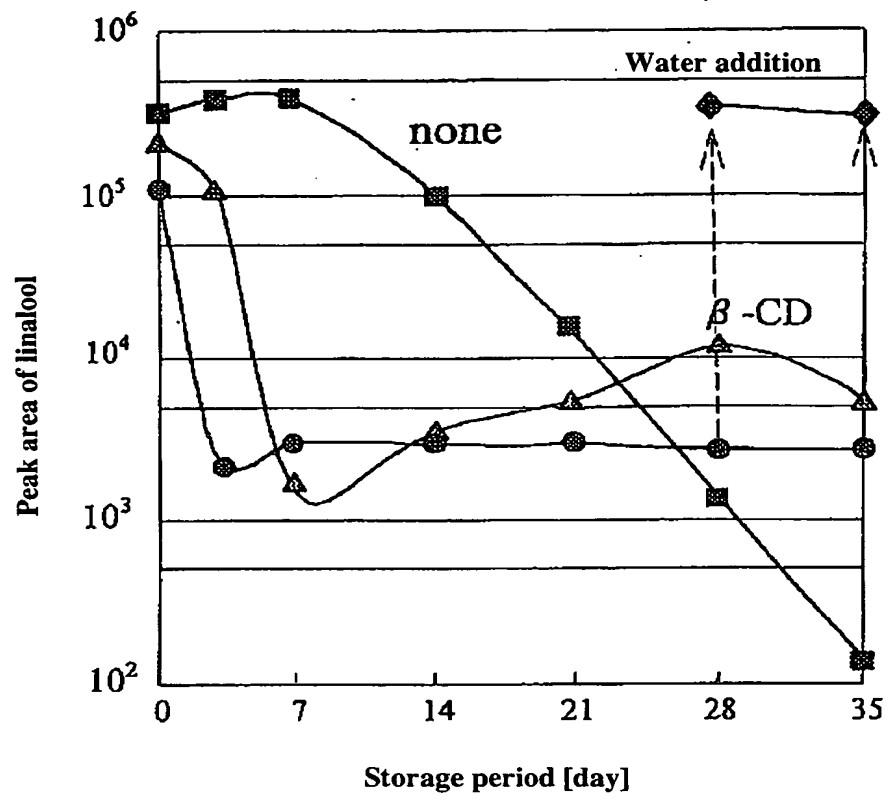
[Fig. 13] An X-ray diffraction chart of a bulky mesoporous powder obtained in the present invention.

[Fig. 14] An X-ray diffraction chart of a rod-shaped mesoporous powder obtained in the present invention.

[Fig. 15] The nitrogen-adsorption isotherm of the mesoporous powder shown in Fig. 14.

[Fig. 16] A chart showing the opening diameter distribution of the mesoporous powder shown in Fig. 14.

Fig. 1



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Fig. 2



Fig. 3



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Fig. 4



Fig. 5



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Fig. 6

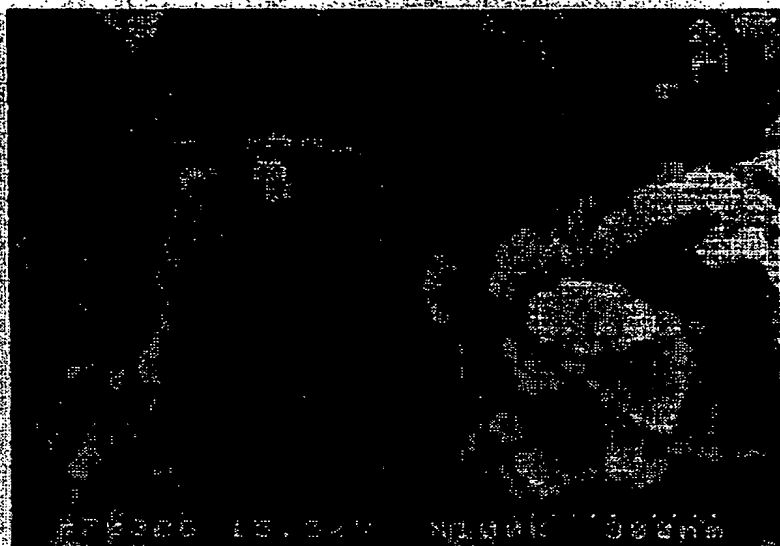
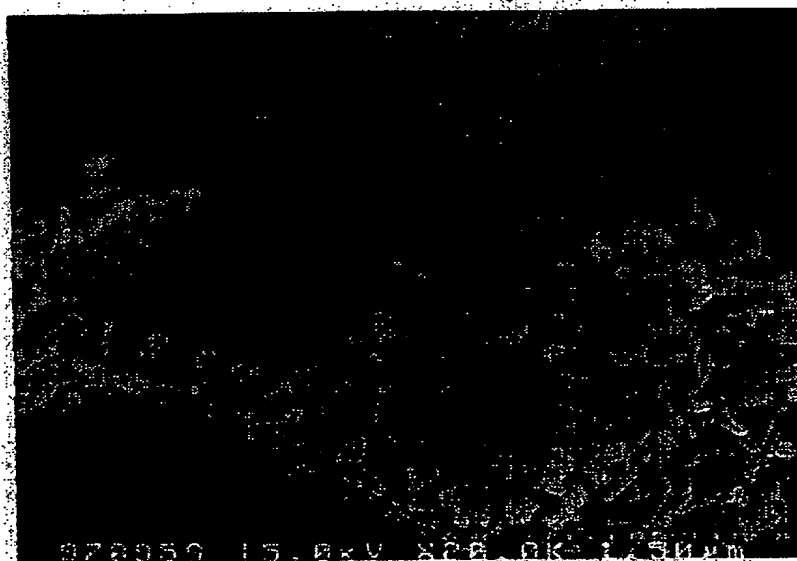


Fig. 7



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Fig. 8



Fig. 9



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Fig. 10

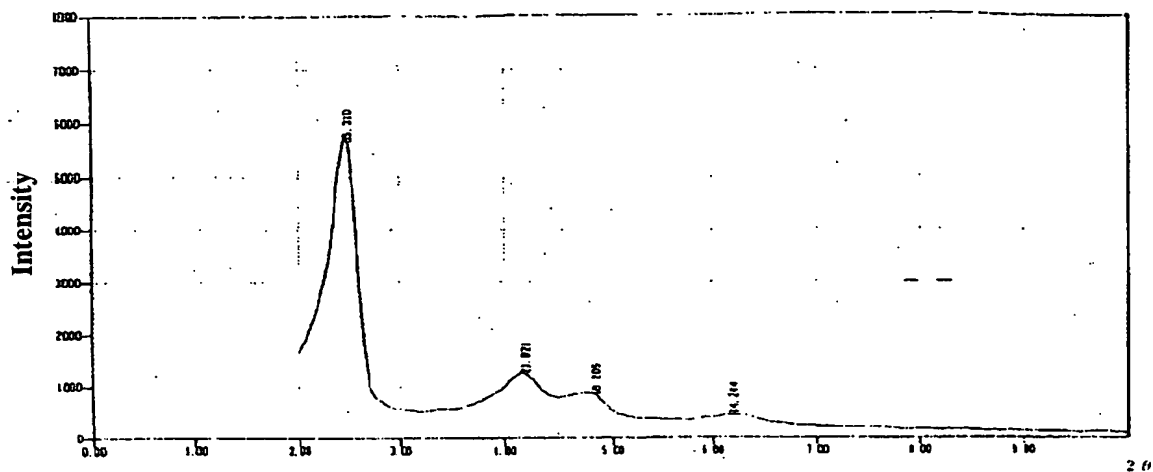
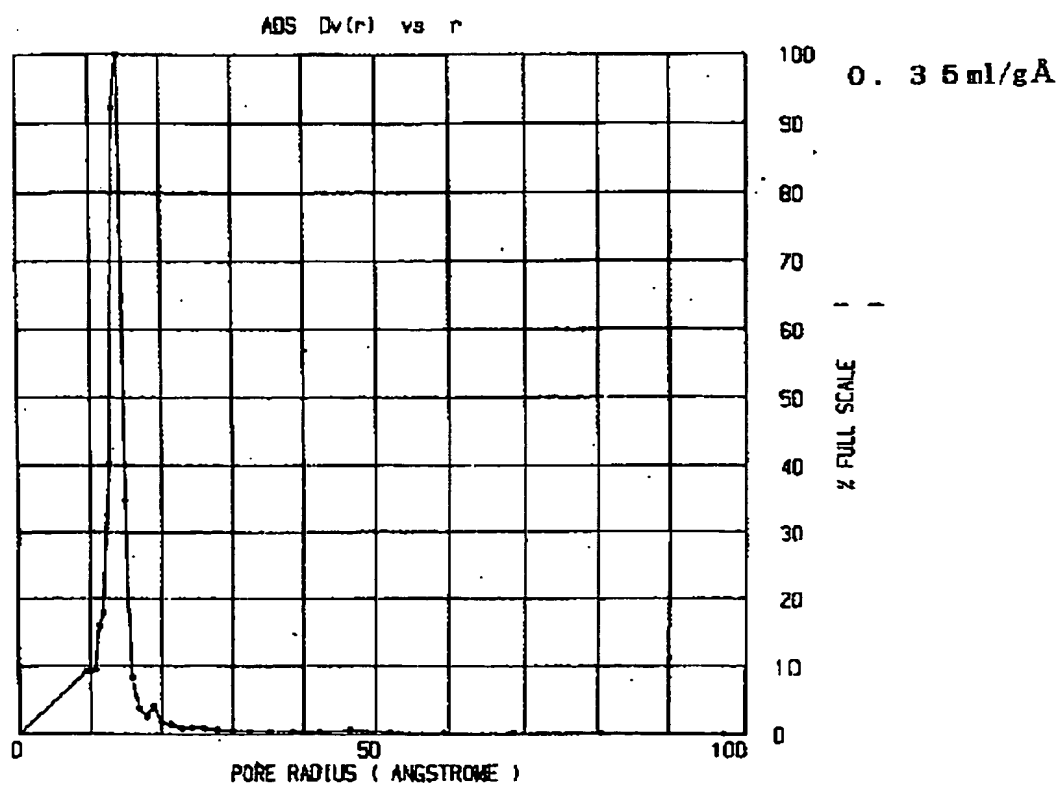
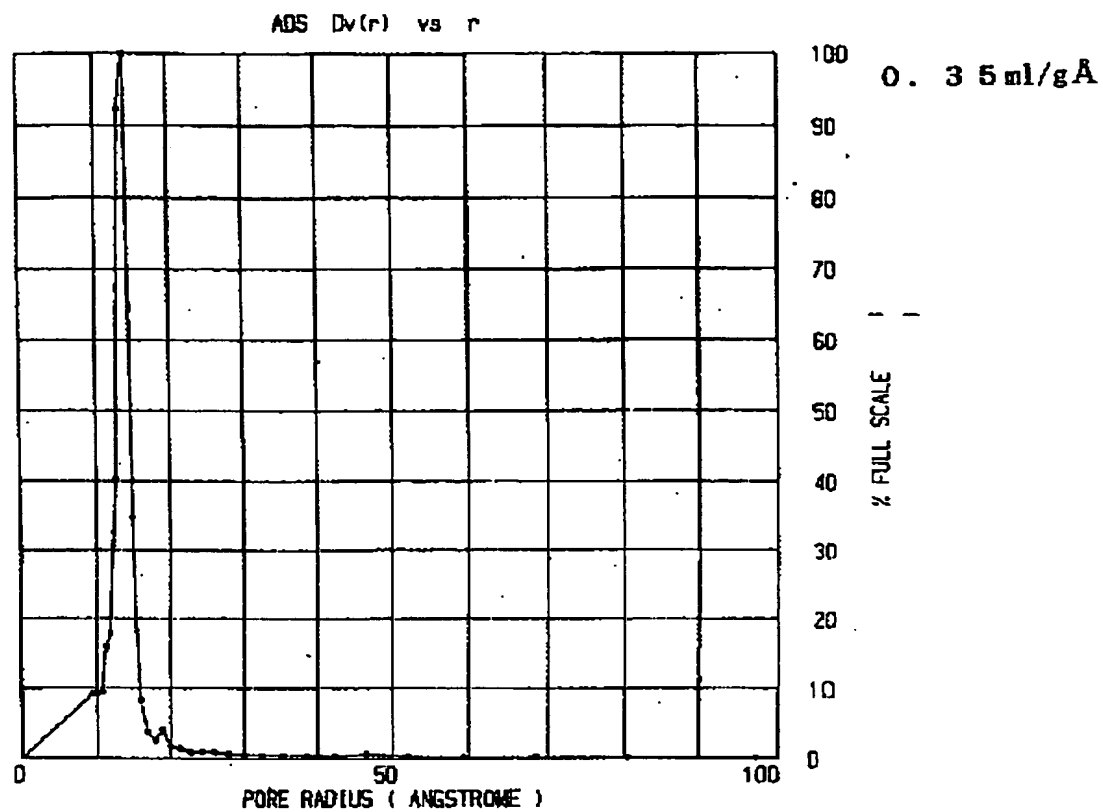


Fig. 11



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Fig. 12



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Fig. 13

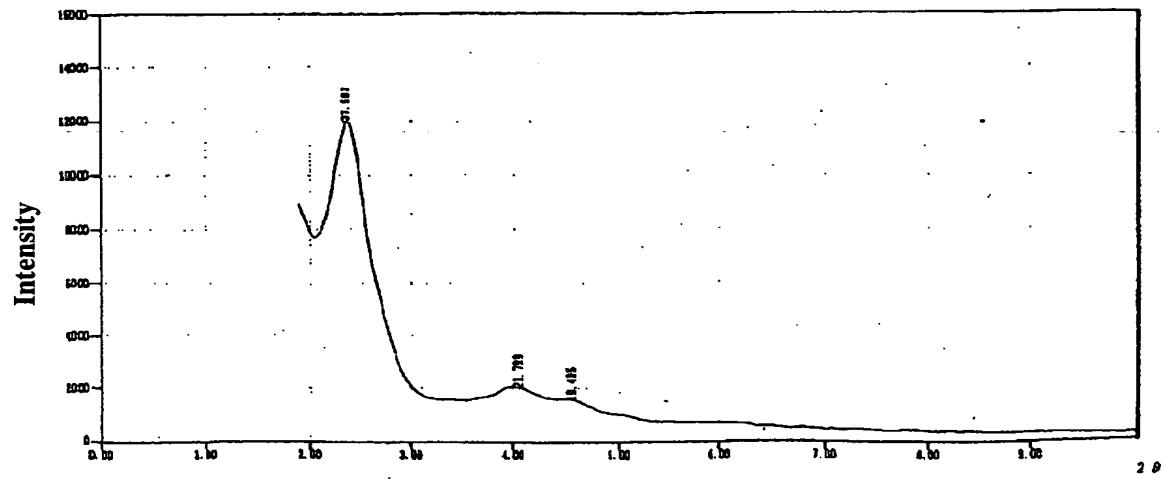


Fig. 14

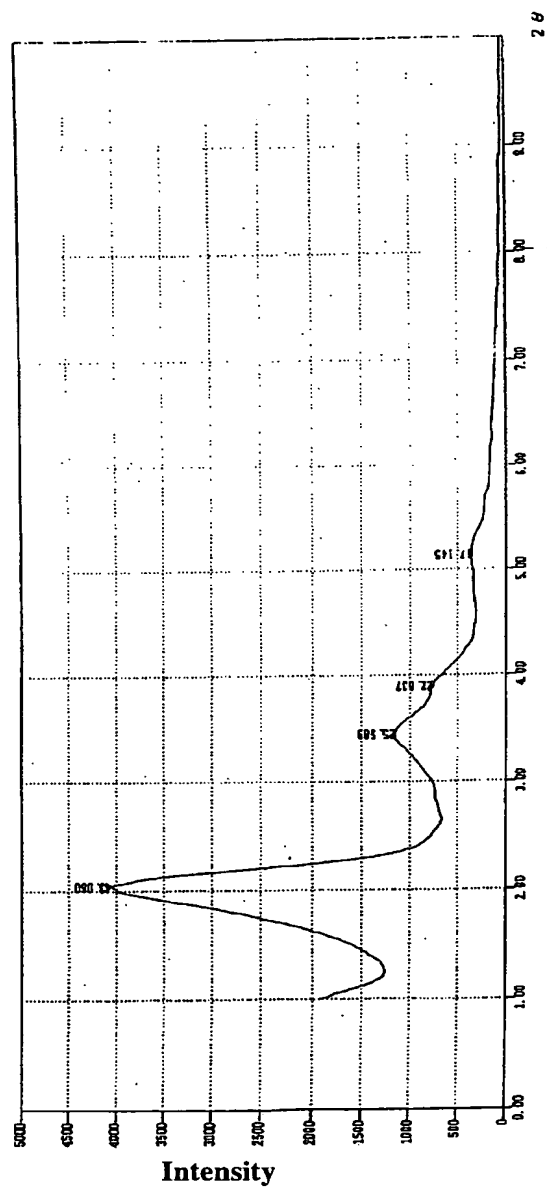


Fig. 15

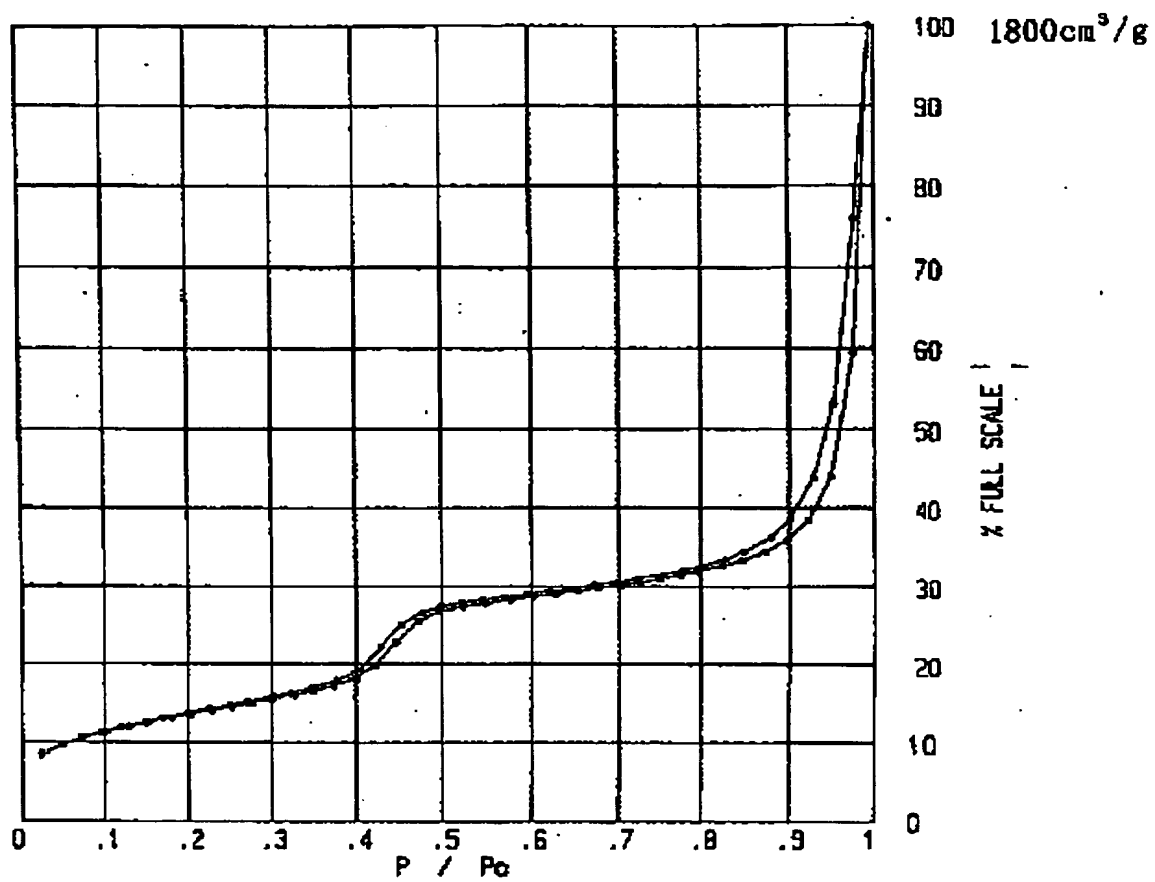
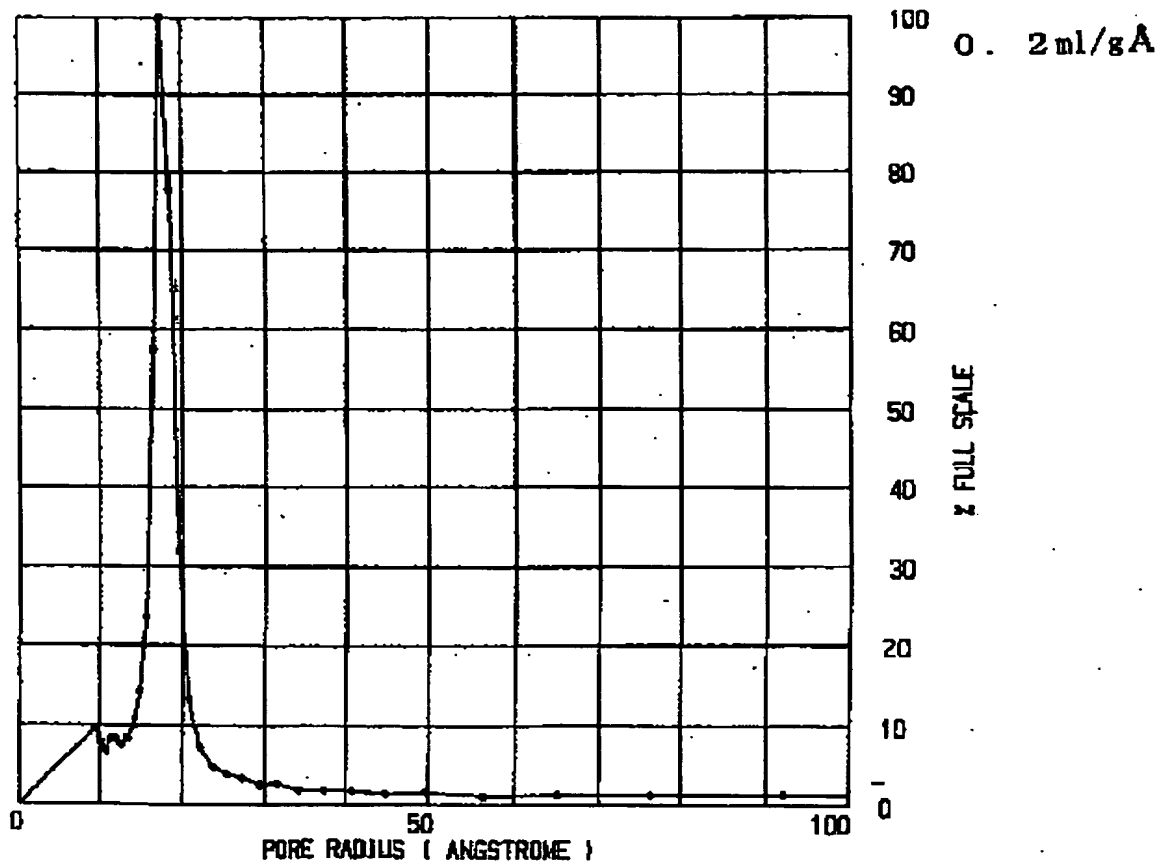


Fig. 16



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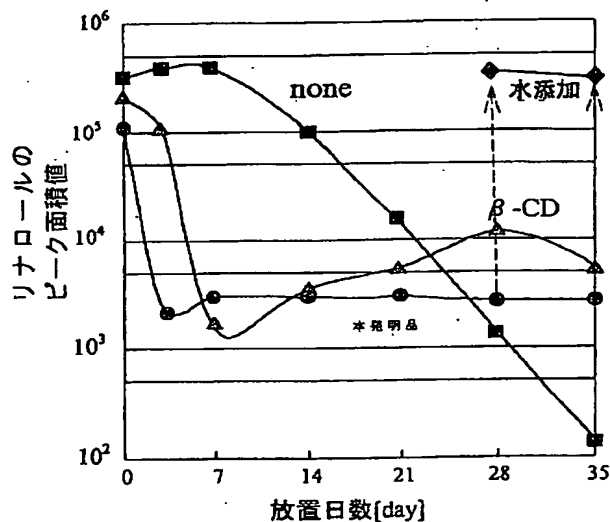
(74) 代理人 弁理士 岩橋 祐司

(54) 【発明の名称】 香料保持粉体及びそれを配合した組成物

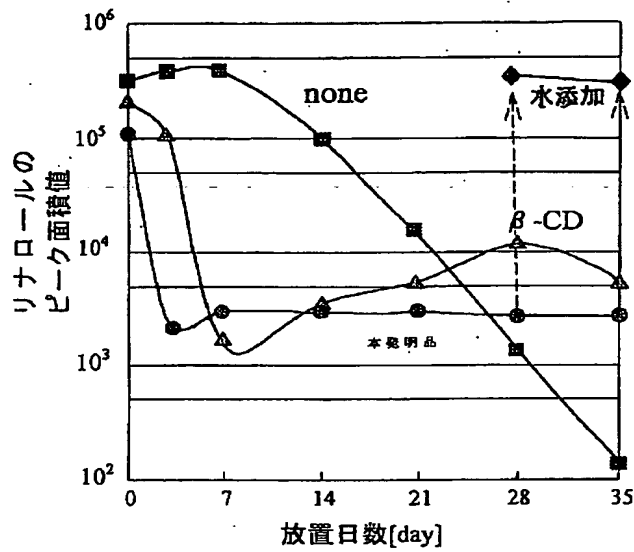
(57) 【要約】

【課題】 本発明の目的は経時的な放散速度の変化が小さく、しかも長時間にわたって香料の保持が可能な香料保持粉体を提供することにある。

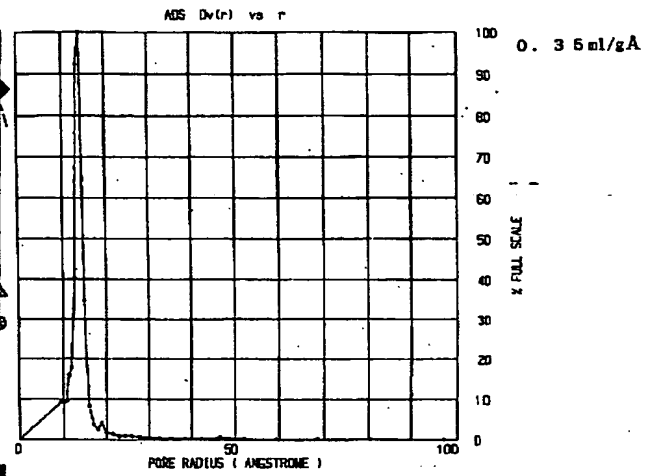
【解決手段】 酸化珪素を主成分としたメソポーラス粉体に香料を保持させたことを特徴とする香料保持粉体及びそれを配合した化粧料。



【図1】

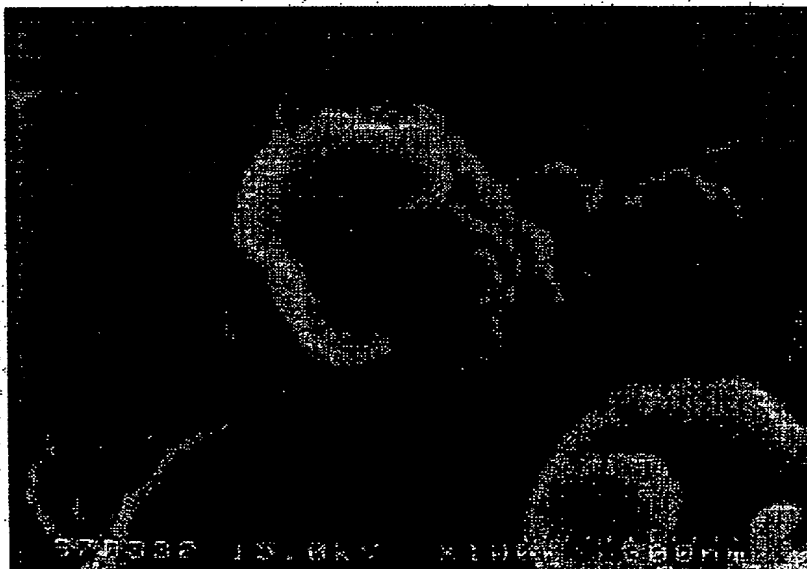


【図12】



【図2】

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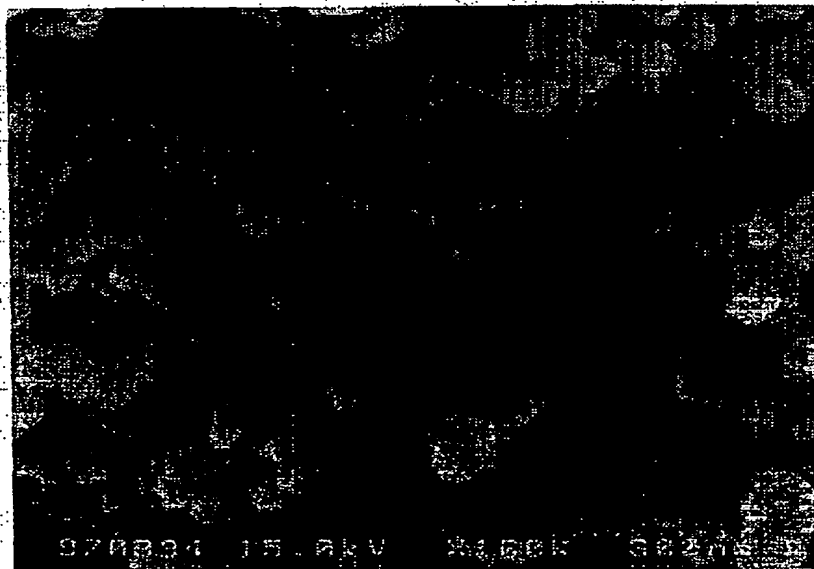
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図面代用写真



【図4】

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【図5】

図面代用写真



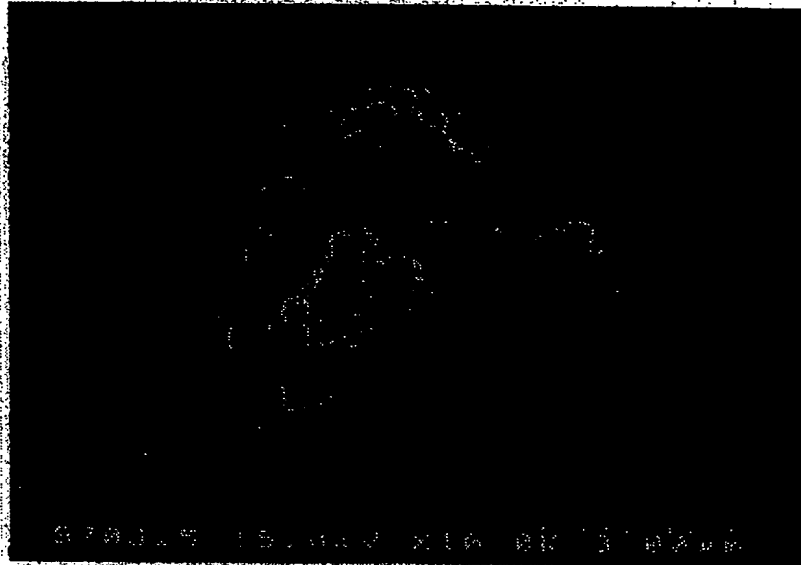
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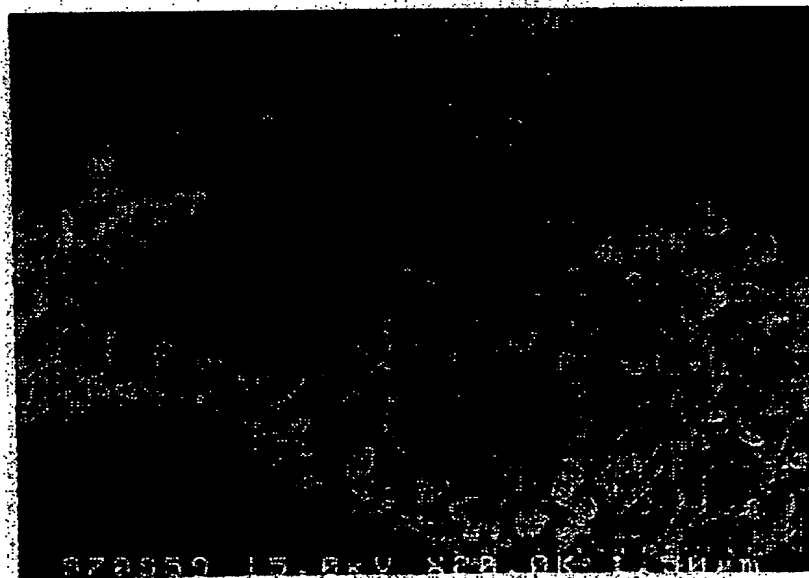
【図 7】

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【図 8】

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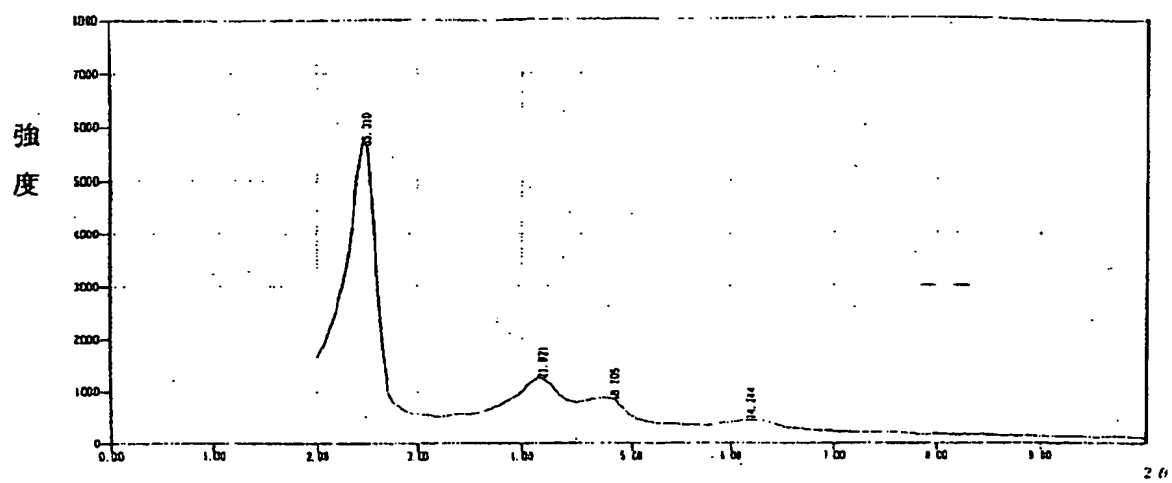


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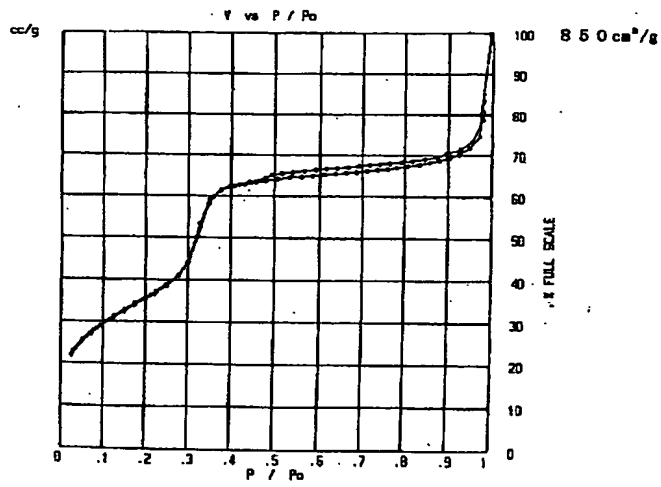
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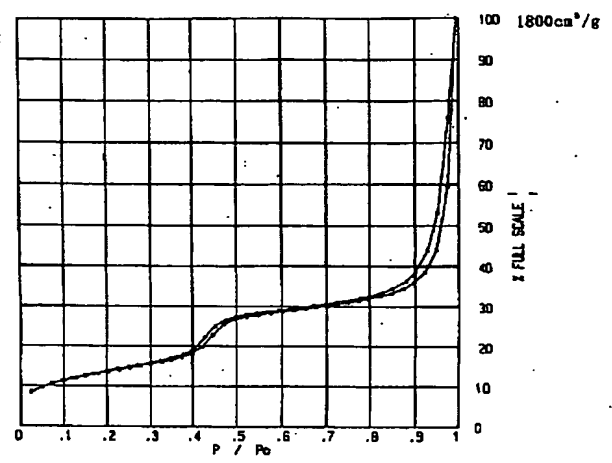
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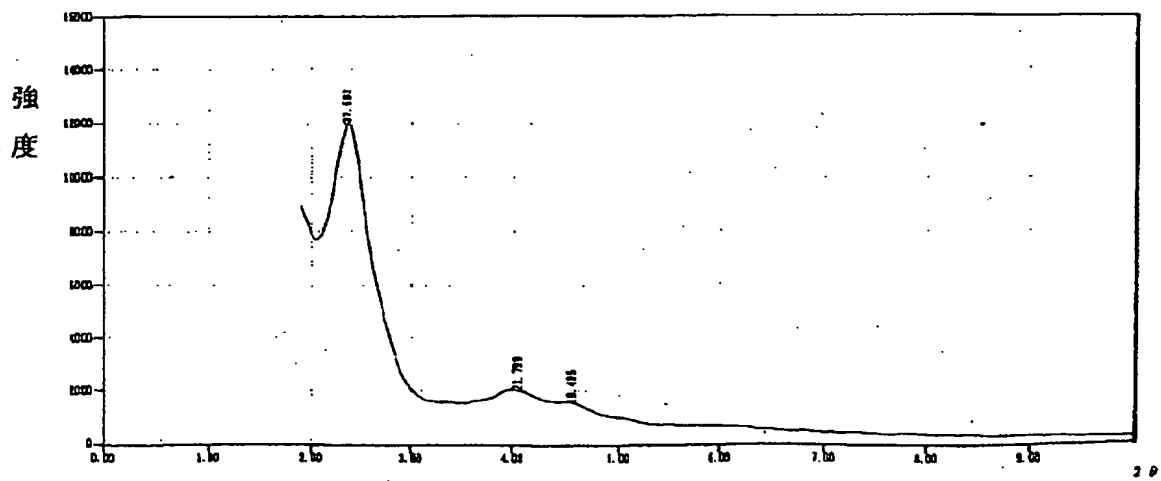
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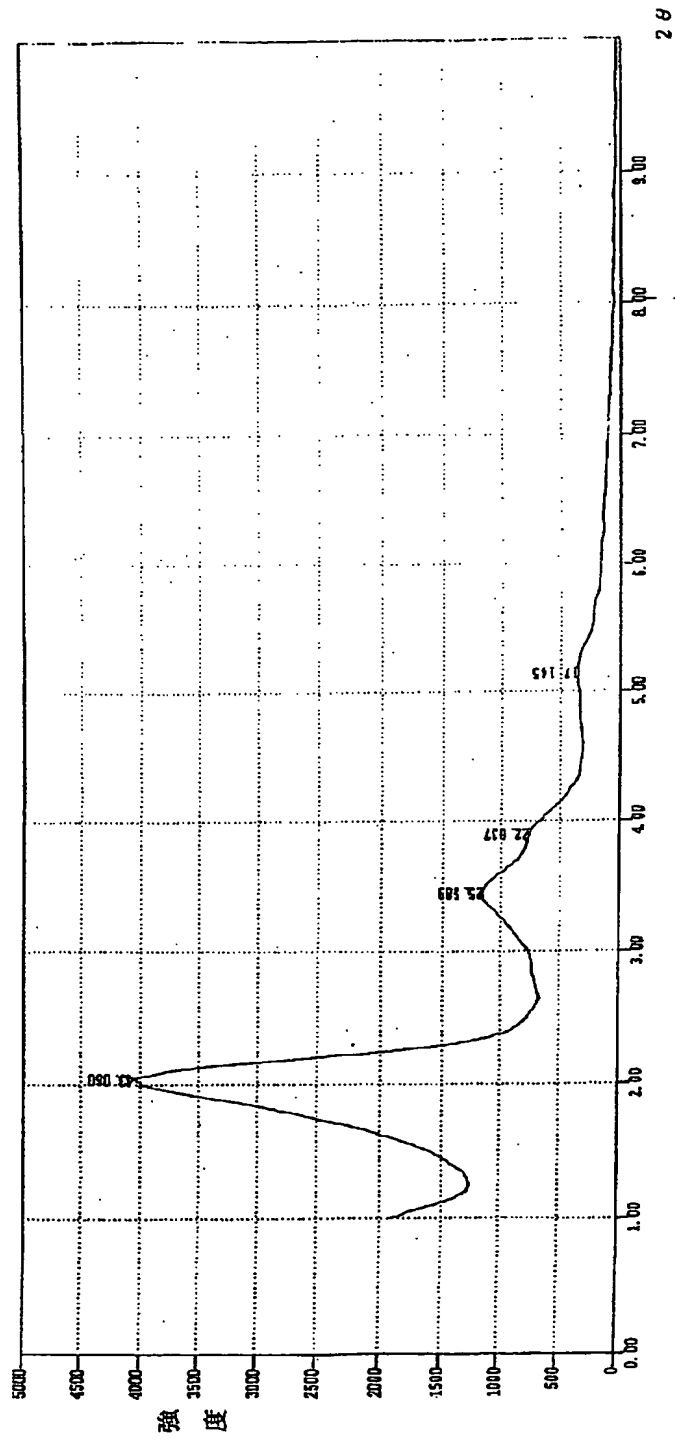
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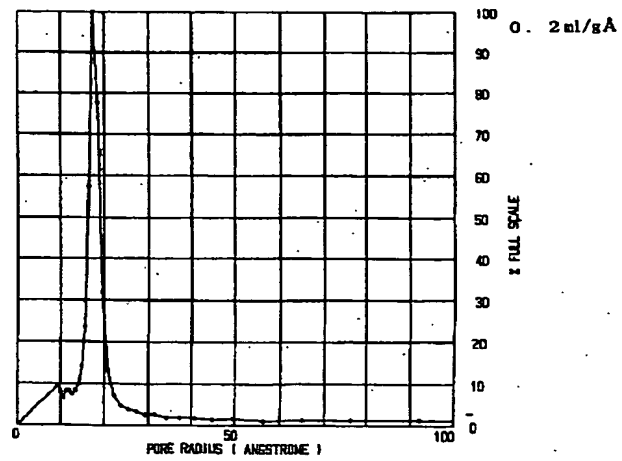
【図13】



【図14】



【図 1 6】



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